PATENT SPECIFICATION

NO DRAWINGS

878,004

Date of Application and filing Complete Specification: April 25, 1960.

No. 14401/60.

Application made in Italy on April 29, 1959.

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Index at acceptance:—Classes 2(6), P2C(8B: 8C: 11: 13B), P2(D1A: FX: K7: T2A), P7C(8B: 8C: 11: 13B: 13C), P7D(1A: 1X: 2A1), P7FX, P7K(2: 7), P7T2A; and 70, Q5X.

International Classification:—C08d. C08c.

COMPLETE SPECIFICATION

ERRATA

SPECIFICATION NO. 878.004

Page 1, line 30, *after* "available" *start new paragraph*

Page 1, line 34, *after* "high" *insert* "-"

Page 3, line 13, *for* "of" *read* "or"

Page 3, line 47, *after* "catalyst" *delete* "polybutadiene"

THE PATENT OFFICE,
20th February, 1962

DS 60799/1(10)/R. 153 200 2/62 PL

ous uses, namely, excellent resistance to abrasion and to ageing by heat and ozone. In addition to these fundamental properties they possess a number of additional advantages, in that they are highly permeable to gases, efficiently withstand light and atmospheric agents, are light in colour and inexpensive, the raw materials required for their manufacture being readily available. However, these copolymers have a low adhesive power and even in admixture with fillers, they tend, on heating, to crumble, instead of becoming pasty, particularly when high molecular copolymers are employed. The above drawbacks hinder bonding of the elastomer to itself or to other materials, and also hinder dispersion of the charges and extrusion.

When the copolymers are of very high molecular weight, the high viscosity consequent thereon (80—100 Mooney and above) makes it difficult to process them in conventional machines for processing natural rubber.

By admixing a base mix of ethylene-propyl- [illegible] moisture and raises the cost of the [illegible] product.

A primary object of this invention is to partially or wholly obviate these drawbacks.

The invention provides a vulcanisable composition comprising a linear substantially amorphous copolymer of ethylene and an alpha-olefin, and a low molecular weight hydrocarbon polymer co-vulcanisable with said copolymer having a viscosity ranging between 500 and 30,000 poises at a temperature of 20° C.

It was found for instance that, by mixing 100 parts of ethylene - propylene copolymer with from 2 to 40 parts of a co-vulcanisable polymer of the above defined viscosity, hence of low molecular weight, thoroughly compact moulded, extruded or calendered articles can be obtained even with machinery which does not appreciably differ from conventional machinery for processing synthetic and natural rubbers.

The following low molecular weight poly-

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International Classification:—C08d. C08c.

COMPLETE SPECIFICATION

Vulcanisable Compositions

We, PIRELLI Societa per Azioni, an Italian Joint Stock Company, of 3 Piazza Duca d'Aosta, Milan, Italy, and MONTECATINI SOCIETA GENERALE PER L'INDUSTRIA MINERARIA E CHIMICA, a Body Corporate organised and existing under the laws of Italy, of 18 Via Filippo Turati, Milan, Italy, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to vulcanisable compositions containing substantially amorphous (non-crystalline) linear copolymers of ethylene with alpha-olefins (otherwise known as 1-olefins), in particular with butene and propylene.

Elastomers containing copolymers of ethylene with alpha-olefins, in particular ethylene-propylene and ethylene-butene copolymers possess highly favourable properties for various uses, namely, excellent resistance to abrasion and to ageing by heat and ozone. In addition to these fundamental properties they possess a number of additional advantages, in that they are highly permeable to gases, efficiently withstand light and atmospheric agents, are light in colour and inexpensive, the raw materials required for their manufacture being readily available. However, these copolymers have a low adhesive power and even in admixture with fillers, they tend, on heating, to crumble, instead of becoming pasty, particularly when high molecular copolymers are employed. The above drawbacks hinder bonding of the elastomer to itself or to other materials, and also hinder dispersion of the charges and extrusion.

When the copolymers are of very high molecular weight, the high viscosity consequent thereon (80—100 Mooney and above) makes it difficult to process them in conventional machines for processing natural rubber.

By admixing a base mix of ethylene-propylene copolymer, whether in admixture with mineral fillers (such as kaolin, calcium carbonate, talc and zinc oxide) or organic fillers (carbon black) or not, with plasticisers such as macro- or micro-crystalline paraffin wax, appreciable advantages are to be found; however, the required quantities of such additives are so high (10—20% of the polymer at least) that some of the properties of the end products are definitely affected. By diluting the polymer as has been proposed with other natural or synthetic rubbers, possibly with a further addition of paraffin, certain properties can be improved, but the amounts of rubber required for this purpose are generally very high, so that certain inherent properties of the ethylene-propylene copolymer are impaired.

By way of example, a 50/50 mix with natural rubber obviously detrimentally affects the ozone-proofness and strength against thermal ageing, increases the tendency to absorb moisture and raises the cost of the end product.

A primary object of this invention is to partially or wholly obviate these drawbacks.

The invention provides a vulcanisable composition comprising a linear substantially amorphous copolymer of ethylene and an alpha-olefin, and a low molecular weight hydrocarbon polymer co-vulcanisable with said copolymer having a viscosity ranging between 500 and 30,000 poises at a temperature of 20° C.

It was found for instance that, by mixing 100 parts of ethylene - propylene copolymer with from 2 to 40 parts of a co-vulcanisable polymer of the above defined viscosity, hence of low molecular weight, thoroughly compact moulded, extruded or calendered articles can be obtained even with machinery which does not appreciably differ from conventional machinery for processing synthetic and natural rubbers.

The following low molecular weight poly-

mers and their mixtures were found excellent in use:

1) liquid depolymerised natural rubber
2) liquid butadiene-styrene copolymer
3) butadiene polymers, in particular those (" Sodium polybutadienes ") obtained by using sodium catalysts, or low molecular weight polymers having a substantially *cis*-1,4 structure obtained by using soluble organo-metallic catalysts.

The invention further provides co-vulcanisable compositions of linear substantially amorphous ethylene - propylene co-polymers with the abovementioned polymers, containing in addition further co-vulcanisable polymers of higher molecular weight, such as natural or synthetic rubbery diene polymers, and similar compositions containing copolymers of ethylene with other alpha-olefins, in particular ethylene-butene copolymers.

The following Example is given to illustrate the invention.

EXAMPLE

The following mixes are prepared in a Banbury mixer at a temperature not exceeding 120° C. thorough mixing and satisfactory dispersion of the charges being obtained in 15 minutes.

Peroxide and sulphur were added at a later stage, after cooling of the mass, in a roll mixer.

TABLE I

	1	2	3	4
Ethylene-propylene or ethylene-butene copolymer containing about 50% mols ethylene and having a Mooney ML viscosity of 87 at 212° F. (100° C.)	100	100	100	100
Calcined kaolin	100	100	—	—
Carbon black FEF (fast extrusion furnace carbon black, a filler)	—	—	35	35
Litharge	1.5	1.5	1.5	1.5
Chlorinated *p*-tertiary butylperoxide	4.0	4.0	4.0	4.0
Sulphur	0.45	0.45	0.45	0.45
Sodium polybutadiene (viscosity 500 poises at 20° C.)	—	20	—	20

Viscosities ascertained on the crude product are as follows:

Mooney ML viscosity at 212° F. (100° C.)	121	45	114	37

The mass was thereupon vulcanised on a press in plate form by heating to 153° C. for 45 minutes.

The mechanical properties of the vulcanisate are as follows:

TABLE 2

	1	2	3	4
Tensile strength ASTM No. D412-51T kg/sq. mm.	0.580	0.540	1.000	1.000
Elongation %	330	350	340	310
Ozone-proofness (ASTM D470-54 T section 43, conc. O_3 0.25/0.3% o)	pass	pass	pass	pass
Permanent deformation ASTM %	5	7	3	4

The Mooney viscosity values above show a favourable plasticizing effect of sodium polybutadiene on the crude mix, and it will be seen in Table 2 that the effect does not impair valuable properties of the vulcanized product (compare columns 2 and 4 with columns 1 and 3 respectively).

The plasticising effect of co - vulcanisable low molecular weight polymers is shown on the following table which indicates the variation in Mooney viscosity as a function of the proportion of sodium polybutadiene added to the ethylene-propylene of ethylene - butene copolymer mentioned above, in the absence of other ingredients:

TABLE 3

	parts per 100 parts copolymer				
sodium polybutadiene	0	2.5	5	10	20
Mooney ML viscosity at 212° F. (100° C.)	88	67	26	20	15

WHAT WE CLAIM IS:—

1. A vulcanisable composition comprising a linear substantially amorphous copolymer of ethylene and an alpha-olefin, and a low molecular weight hydrocarbon polymer co-vulcanisable with said copolymer having a viscosity ranging between 500 and 30,000 poises at a temperature of 20° C.

2. A composition as claimed in claim 1, wherein the copolymer is an ethylene-propylene or ethylene - butene copolymer.

3. A composition as claimed in claim 1 or claim 2, comprising in addition a further co-vulcanisable copolymer having a higher molecular weight than said co-vulcanisable polymer.

4. A composition as claimed in any of the preceding claims, wherein the co-vulcanisable polymer is present in an amount of from 2 to 40 parts by per 100 parts by weight of the copolymer of ethylene with an alpha-olefin.

5. A composition as claimed in any of the preceding claims, wherein the co-vulcanisable polymer is liquid depolymerised natural rubber, a liquid butadiene-styrene copolymer, a polybutadiene or a mixture of two or more thereof.

6. A composition as claimed in any of claims 3 to 5, wherein the co-vulcanisable polymer is a polybutadiene obtained by using a sodium catalyst polybutadiene.

7. A vulcanisable composition substantially as herein described with reference to the foregoing Example.

8. Vulcanised articles obtained from a composition as claimed in any one of the preceding claims.

Pirelli Societa per Azioni and Montecatini Societa Generale per l'Industria Mineraria e Chimica.

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Chartered Patent Agents.

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